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(54) TWO-COMPONENT PAINT SYSTEM

(54) SYSTEME DE PEINTURE A DEUX CONSTITUANTS

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ABSTRACT:

The invention relates to a paint system composed of two components (I) and (II), which is characterized in that component (I) comprises
(A) from 5 to 50% by weight of at least one binder,
(B) from 0 to 20% by weight of at least one cross linking agent,
(C) from 0.5 to 60% by weight of at least one pigment,
(D) from 5 to 80% by weight of water,
(E) from 0 to 40% by weight of at least one organic solvent,
(F) from 0 to 5% by weight of at least one rheology controlling additive, and
(G) from 0 to 10% by weight of at least one further conventional paint auxiliary, the sum of the percentages by weight indicated for components (A), (B), (C), (D), (E), (F) and (G) always being 100% by weight, and component (II) comprises
(H) from 70 to 99% by weight of water,
(J) from 0 to 10% by weight of at least one organic solvent,
(K) from 0.1 to 10% by weight of at least one rheology-controlling additive, and
(L) from 0 to 10% by weight of at least one further conventional paint auxiliary, the sum of the percentages by weight indicated for components (H), (J), (R) and (L) always being 100% by weight.

CLAIMS: Show all claims

*** Note: Data on abstracts and claims is shown in the official language in which it was submitted.

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Pat nt Claims

1. Paint system composed of two components (I) and (II), characterized in that component (I) comprises

(A) from 5 to 50% by weight of at least one binder,

(B) from 0 to 20% by weight of at least one crosslinking agent,

(C) from 0.5 to 60% by weight of at least one pigment,

(D) from 5 to 80% by weight of water,

(E) from 0 to 40% by weight of at least one organic solvent

(F) From 0 to 5% by weight of at least one rheology-controlling additive, and

(G) from 0 to 10% by weight of at least one further conventional paint auxiliary,

the sum of the percentages by weight indicated for compon nts (A), (B), (C), (D), (E), (F), and (G)

always being 100% by weight, and component (II) comprises

(H) from 70 to 99% by weight of water,

(J) from 0 to 10% by weight of at least one organic solvent,

(K) from 0.1 to 10% by weight of at least one rheology-controlling additive, and

(L) from 0 to 10% by weight of at least one further conventional paint auxiliary,

the sum of the percentages by weight indicated for components (H), (J), (K), (J) and (L) always being 100% by weight.

2. Paint system according to claim 1, characterized in that constituent (A) consists of at least one water-dilutable polyurethane resin or of a mixture of at least one water-dilutable polyurethane resin and at least one water-dilutable polyester resin and/or at least one water-dilutable polyacrylate resin.

3. Paint system according to claim 1 or 2, characterized in that constitu nt (B) consists f

at least on amino resin or of at least one block d polyisocyanate or of a mixture of at least one amino resin and at least on blocked polyisocyanate.

4. Paint system according to one of claims 1 to 3, characterized in that constituent (K) is an inorganic phyllosilicate.

5. Use of a paint system according to one of claims 1 to 4 for the production of automotive refinishes.

6. Use of a paint system according to one of claims 1 to 4 for the production of paints for plastics substrates

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Two-component paint system

The invention relates to a paint system composed of two components and to the use of this paint system for the production of automotive refinishes.

DE-A-41 10 520 describes a mixer system for the production of aqueous automotive refinishes, which system involves automotive refinishes being produced by mixing a pigment-containing base color, which contains less than 5% by weight of water, with a pigment-free aqueous component.

In the two-component paint system described in DE-A-41 10 520 the pigment-containing base colors have unfavorable flow characteristics, which have an adverse effect both on meterability and on miscibility with the pigment-free aqueous component. One of the consequences of this is that the precise matching of predetermined colors is rendered more difficult.

The object of the present invention is to provide a paint system composed of two components which does not have the disadvantages described above.

This object is achi ved by the provision of a paint system compos d of two components (I) and (II), which is characterized in that component (I) comprises

(A) from 5 to 50%, preferably from 10 to 30%, by weight of at least one binder

(B) from 0 to 20% , preferably from 0 to 5%, by weight of at least one crosslinking agent,

(C) from 0.5 to 60%, preferably from 0.5 to 40%, by weight of at least one pigment

(D) from 5 to 80%, preferably from 10 to 70%, by weight of water

(E) from 0 to 40%, preferably from 5 to 20%, by weight of at least one organic solvent,

(F) from 0 to 5%, preferably from 0 to 2%, by weight of at least one rheology-controlling additive, and

(G) from 0 to 10%, preferably from 2 to 5%, by weight of at least one further conventional paint auxiliary,

th sum of the percentages by weight indicated for components (A), (B), (C), (D), (E), (F) and (G) always b ing 100% by w ight, and component (II) compris s

(H) from 70 to 99%, preferably from 80 to 99%, by weight of water

(J) from 0 to 10%, preferably from 0 to 2%, by weight of at least one organic solvent,

(K) from 0.1 to 10%, preferably from 1 to 3%, by weight of at least one rheology-controlling additive, and

(L) from 0 to 10%, preferably from 0.5 to 3%, by weight of at least one further conventional paint auxiliary,

the sum of the percentages by weight indicated for components (H), (J), (K) and (L) always being 100% by weight.

The advantages of the two-component paint system provided in accordance with the invention are in particular that the components are readily meterable and miscible, making the production of paints having predetermined colors very easy. In many cases it is no long r nec ssary to formulate th paints produced using

the paint system according to the invention to processing viscosity in an additional operation. A further advantage lies in the high freeze-thaw stability of component (I).

As constituent (A) in component (I) it is possible to employ all water-soluble or water-dispersible binders which are suitable for paints. In particular it is possible to employ water-soluble or water-dispersible polyurethane resins, polyester resins, polyacrylate resins, polyacrylate resins prepared in the presence of polyurethane and/or polyester resins, or mixtures of these resins as constituent (A) in component (I).

Examples of suitable polyurethane resins are described in the following documents: EP-A-355 433, DE-A-35 45 618, DE-A-38 13 866. [sic] DE-A-32 10 051, DE-A-26 24 442, DE-A-37 39 332, US-A-4,719,132, EP-A-89 497, US-A-4,558,090, US-A-4,489,135,, [sic] DE-A-36 28 124, EP-A-158 099, DE-A-29 26 584, EP-A-195 931, DE-A-33 21 180 and DE-A-40 05 961.

As constituent (A) in component (I) it is preferred to employ polyurethane resins which have a number-average molecular weight (determined by gel permeation chromatography using polystyrene as standard) of from 1000 to 30,000, preferably from 1500 to 20000, and an acid number of from 5 to 70 mg of KOH/g, preferably

from 10 to 30 mg of KOH/g, and which can be pr pared by reacting prepolymers which contain isocyanate groups with compounds which ar reactive toward isocyanate groups.

The preparation of prepolymers containing isocyanate groups can be effected by reacting polyols having a hydroxyl number of from 10 to 1800 mg, preferably from 50 to 1200 mg of KOH/g, with excess polyisocyanates at temperatures of up to 150°C, preferably from 50 to 130°C, in organic solvents which are incapable of reacting with isocyanates. The ratio of equivalents of NCO to OH groups is between 2.0:1.0 and > 1.0:1.0, preferably between 1.4:1 and 1.1:1.

The polyols employed for the preparation of the prepolymer may be of low and/or high molecular weight and may contain groups which are slow to react and are anionic or are capable of forming anions. It is also possible to make partial use of low molecular weight polyols having a molecular weight of from 60 to 400 in order to prepare the prepolymers which contain isocyanate groups, in which case quantities of up to 30% by weight of the overall polyol constituents, preferably from about 2 to 20% by weight, are employed. To obtain an NCO prepolymer of high flexibility a high proportion should be added of a predominantly linear polyol having a preferr d OH number of from 30 to

150 mg of KOH/g. Up to 97% by w ight of the overall polyol may consist of saturated and unsaturat d polyesters and/or polyethers having a molecular mass Mn of from 400 to 5000. The polyether diols chosen should not introduce excessive quantities of ether groups, since otherwise the polymers formed swell in water. Polyester diols are prepared by esterification of organic dicarboxylic acids or their anhydrides with organic diols, or are derived from a hydroxycarboxylic acid or from a lactone. In order to prepare branched polyester polyols, a minor proportion of polyols or polycarboxylic acids having a higher functionality can be employed.

Typical multifunctional isocyanates which are employed are aliphatic, cycloaliphatic and/or aromatic polyisocyanates having at least two isocyanate groups per molecule. Preference is given to the isomers or isomer mixtures of organic diisocyanates. Because of their good resistance to ultraviolet light, (cyclo)aliphatic diisocyanates give products having a low tendency to yellowing. The polyisocyanate component used to form the prepolymer may also contain a proportion of polyisocyanates of higher functionality, provided that this does not bring about any gelling. Products which have proven suitable as triisocyanates are those obtained by trimerization or oligomerization of diisocyanates or by reaction of diisocyanates with

polyfunctional compounds which contain OH or NH groups. If desired, the average functionality can be lowered by addition of monoisocyanates.

Examples of polyisocyanates which can be employed are phenylene diisocyanate, tolylene diisocyanate, xylylene diisocyanate, bisphenylene diisocyanate, naphthylene diisocyante, diphenylmethane diisocyanate, isophorone diisocyanate, cyclopentylene diisocyanate, cyclohexylene diisocyanate, methylcyclohexylene diisocyanate, dicyclohexylmethane diisocyanate, trimethylene diisocyanate, tetramethylene diisocyanate, pentamethylene diisocyanate, hexamethylene diisocyanate, propylene diisocyanate, ethylethylene diisocyanate and trimethylhexane diisocyanate.

Polyurethanes are generally incompatible with water unless during their synthesis specific constituents are incorporated and/or particular preparation steps are carried out. Thus, in order to prepare the polyurethane resins, it is possible to use compounds which contain two H-active groups which are reactive with isocyanate groups, and at least one group which ensures dispersibility in water. Suitable groups of this kind are nonionic groups (e.g. polyethers), anionic groups, mixtures of these two groups, or cationic groups.

To introduce anionic groups into polyur thane resin molecules, compounds ar us d which contain at least one group which is reactive toward isocyanat groups and at least one group which is capable of forming anions. Suitable groups which are reactive toward isocyanate groups are in particular hydroxyl groups, and also primary and/or secondary amino groups. Groups capable of forming anions are carboxyl, sulfonic acid and/or phosphonic acid groups. Preference is given to employing alkanoic acids having two substituents on the α carbon atom. The substituent may be a hydroxyl group, an alkyl group or an alkylol group. These polyols have at least one, generally from 1 to 3, carboxyl groups in the molecule. They have from two to about 25, preferably from 3 to 10 carbon atoms. The carboxyl-containing polyol may make up from 3 to 100% by weight, preferably from 5 to 50% by weight, of the overall polyol constituent in the NCO prepolymer.

The isocyanate groups of the prepolymer which contains isocyanate groups are reacted with a modifying agent. In this context the modifying agent is preferably added in a quantity so as to result in chain extensions and therefore in increases in molecular weight. The modifying agents preferably employed are organic compounds which contain hydroxyl and/or secondary and/or primary amino groups, especially di-, tri- and/or polyols of higher functionality. Exampl [sic]

of polyols which can b employed ar trimethylol-propan , 1,3,4 butanetriol [sic], glycerol, erythritol, mesoerythritol, arabitol, adonitol, tc. Trimethylolpropane is preferably employed.

As constituent (A) in component (I) it is possible in principle to employ all water-soluble or water-dispersible polyacrylate resins which are suitable for aqueous paints. A very large number of such resins has been described, and a very wide selection of them is available commercially. Particularly suitable polyacrylate resins are described in DE-A-38 32 826 and in DE-A-38 41 540.

As constituent (A) in component (I) it is also possible to employ water-soluble or water-dispersible polyester resins.

As constituent (B) in component (I) it is possible, for example, to employ blocked polyisocyanates and/or water-soluble or water-dispersible amino resins. It is preferred - if desired in the presence of cosolvents - to employ water-soluble or water-dispersible melamine resins. These are in general etherified melamine/formaldehyde condensation products. The solubility or dispersibility in water of the amino resins depends, apart from the degree of condensation, which should be as low as possible, on th eth rifying

component, with only the lowest members of the alcohol or of the ethylene glycol monoether series giving condensation products which are soluble in water. The melamine resins which are etherified with methanol have the greatest significance. If solubilizers are used, it is also possible to disperse butanol-etherified melamine resins in the aqueous phase. The possibility also exists of incorporating carboxyl groups into the condensation product. Transetherification products of highly etherified condensation products of formaldehyde with hydroxycarboxylic acids, via their carboxyl groups, are soluble in water after neutralization.

As constituent (C), components (I) may contain all conventional paint pigments which do not react with water or dissolve in water. The pigments may comprise inorganic or organic compounds and may be effect pigments and/or color pigments. In order to ensure a degree of applicability which is as close as possible to universal, and in order to maximize the possible colors, it is preferred to incorporate, in one component (I), either only color pigments or only effect pigments, but not mixtures of color and effect pigments.

Effect pigments which can be employed are metal flake pigments such as commercial aluminum bronzes, aluminum bronzes chromated in accordance with DE-A-36 36 183,

and commercial stainless-steel bronzes, and also nonmetallic effect pigments such as, for example, pearlescent or interference pigments. Examples of suitable inorganic color pigments are titanium dioxide, iron oxides, Sicotrans yellow and carbon black. Examples of suitable organic color pigments are indanthrene blue, Cromophthal red, Irgazin orange and Heliogen green.

As constituent (E), component (I) may contain at least one organic solvent. Examples of suitable solvents are in particular water-miscible solvents such as, for example, alcohols, esters, ketones, keto esters, glycol ether esters and the like. Alcohols and glycol ethers are preferably employed, and butyl glycol and butanols are particularly preferred.

As constituent (F) component (I) may contain at least one rheology-controlling additive. Examples of rheology-controlling additives are crosslinked polymer microparticles as disclosed, for example, in EP-A-38 127, inorganic phyllosilicates, for example aluminum-magnesium silicates, sodium-magnesium phyllosilicates and sodium-magnesium-fluorine-lithium phyllosilicates of the montmorillonite type, and also synthetic polymers containing ionic groups and/or groups which have an associated action, such as polyvinyl alcohol, poly(meth)acrylamide,

poly(meth)acrylic acid, polyvinylpyrrolidon , styr ne/maleic anhydrid or ethyl ne/mal ic anhydride copolymers and derivatives thereof, or els hydrophobically modified, ethoxylated urethanes or polyacrylates. As rheology-controlling additives it is preferred to employ inorganic phyllosilicates. Particular preference is given to employing, as rheology-controlling additive, a combination of a polyacrylate resin which contains carboxyl groups, having an acid number of from 60 to 780 mg, preferably from 200 to 500 mg of KOH/g, with a sodium-magnesium phyllosilicate.

The sodium-magnesium phyllosilicate is expediently incorporated into the paint component in the form of an aqueous paste. The paste preferably contains 3% by weight of phyllosilicate and 3% by weight of polypropylene glycol or 2% by weight of phyllosilicate and 0.6% by weight of polypropylene glycol or 2% by weight of phyllosilicate and 2% by weight of other commercial, surface-active substances, all percentages being based on the overall weight of the paste. Component (I) of the paint system according to the invention should preferably not contain any rheology-controlling additive, especially not any inorganic phyllosilicate as rheology-controlling additive. The rheology-controlling additives which are necessary for th paints which can b prepared using the paint system

according to th invention should pr f rably b contained xclusively in component (II). It is particularly preferred that, in the cas s in which an inorganic phyllosilicate is employed as rheology-controlling additive, the inorganic phyllosilicate is exclusively contained in paint component (II).

As well as constituent (F), component (I) may also contain, as constituent (G), at least one further conventional paint additive. Examples of such additives are antifoams, dispersion auxiliaries, emulsifiers and leveling assistants.

Component (I) is prepared by methods known to the person skilled in the art by mixing and, if desired, dispersing the individual constituents. Thus, for example, color pigments are conventionally incorporated by dispersion of the respective pigments in one or more binders. The dispersion of the pigments is carried out using conventional devices such as, for example, bead mills and sand mills.

The effect pigments are conventionally incorporated by homogeneous mixing of the effect pigments with one or more solvents. This mixture is then, using a stirrer or dissolver, stirred into a mixture of one or more of the above-described binders, if desired with the addition of furth r organic solv nts.

Constitu nts (J), (K) and (L) of paint component (II) correspond to constituents (E), (F) and (G) of paint component (I).

The paint system according to the invention is suitable for the production of aqueous paints which are intended to have a color determined precisely beforehand. By mixing correspondingly pigmented paint components (I) in proportions which are necessary to achieve the corresponding colors, and adding paint component (II), it is possible to obtain aqueous paints which are accurate in color and can be processed immediately. The paint system according to the invention is particularly suitable for mixer systems for production of automotive refinishes (cf. e.g. Glasurit-Handbuch, 11th Edition, Kurt R., [sic] Vincentz-Verlag, Hanover 1984, pages 544 to 547). Using the paint system according to the invention it is of course also possible to produce paints for other areas of application, for example the painting of plastics or the production-line finishing of motor vehicle bodies.

The invention is illustrated in more detail below with reference to exemplary embodiments. In these embodiments all indications as to parts and percentages are by weight, unless expressly noted otherwise.

1. Preparation of an organic polyurethane resin solution

686.3 g of a polyester having a number-average molecular weight of 1400 based on a commercial unsaturated dimeric fatty acid (having an iodine number of 10 mg of I_2/g, a monomer content of not more than 0.1%, a trimer content of not more than 2%, an acid number of from 195 to 200 mg of KOH/g and a hydrolysis number of from 197 to 202 mg of KOH/g), isophthalic acid and hexanediol are placed under protective gas in an appropriate reaction vessel with stirrer, reflux condenser and feed vessel, and 10.8 g of hexanediol, 55.9 g of dimethylolpropionic acid, 344.9 g of methyl ethyl ketone and 303.6 g of 4,4'-di-(isocyanato-cyclohexyl) methane are added in succession. This mixture is maintained under reflux until the isocyanate content has fallen to 1.0%. Subsequently 26.7 g of trimethylolpropane are added to the mixture, which is maintained under reflux to a viscosity of 12 dPas (for a solution of one part of resin solution in one part of N-methylpyrrolidone). 1378.7 g of butylglycol are then added. After a vacuum distillation in which the methyl ethyl ketone is removed, the resin solution is neutralized with 32.7 g of dimethylethanolamine. The solids content of the resulting resin solution is 44%. Under intensive stirring, it is diluted to a solids content of 41% by w ight by adding butylglycol.

2. Preparation of an aqueous polyur thane resin dispersion

686.3 g of a polyester having a number-average molecular weight of 1400 based on a commercial unsaturated dimeric fatty acid (having an iodine number of 10 mg of I_2/g, a monomer content of not more than 0.1%, a trimer content of not more than 2%, an acid number of from 195 to 200 mg of KOH/g and a hydrolysis number of from 197 to 202 mg of KOH/g), isophthalic acid and hexanediol are placed under protective gas in an appropriate reaction vessel with stirrer, reflux condenser and feed vessel, and 10.8 g of hexanediol, 55.9 g of dimethylolpropionic acid, 344.9 g of methyl ethyl ketone and 303.6 [lacuna] of 4,4'-di-(isocyanatocyclohexyl) methane are added in succession. This mixture is maintained under reflux until the isocyanate content has fallen to 1.0%. Subsequently 26.7 g of trimethylolpropane are added to the mixture, which is maintained under reflux to a viscosity of 12 dPas (for a solution of one part of resin solution in one part of N-methylpyrrolidone). Any excess isocyanate present is destroyed by adding 47.7 g of butylglycol. Subsequently 32.7 g of dimethylethanol-amine, 2688.3 g of deionized water and 193.0 g of butylglycol are added to the reaction mixture with vigorous stirring. After the removal of the methyl ethyl ketone by vacuum distillation, an aqu ous

dispersion is obtained which has a solids content of about 27%.

3. Preparation of pigment pastes

3.1 Preparation of a pigment paste containing aluminum pigment

15.5 parts of an aluminum bronze chromated in accordance with DE-A-36 36 183 (aluminum content 65%, average particle diameter 15 µm) are homogeneously dispersed in 14 parts of butylglycol by stirring for 15 minutes and then run with stirring into a mixture of 51 parts of the polyurethane resin solution prepared according to section 1., 19.5 parts of a commercial, methanol-etherified melamine resin (75% in isobutanol) and 10 parts of butylglycol. This mixture is stirred for a further 30 minutes using a high-speed stirrer at 1000 rpm.

3.2 Preparation of a blue-pigmented pigment paste

7 parts of Paliogen blue, 57 parts of the polyurethane resin solution prepared according to section 1., 15 parts of butylglycol and 21 parts of a commercial, methanol-etherified melamine resin (75% in isobutanol) are mixed with stirring and dispersed in a sand mill.

4. Preparation of components (I) according to the invention

4.1 Preparation of component (I)-1

30 parts of the pigment paste prepared according to section 3.1 are mixed thoroughly with 40 parts of the aqueous polyurethane resin dispersion prepared according to section 2. and 30 parts of deionized water. The component (I) obtained in this way is readily meterable, can be mixed very well with components (I) pigmented with other colors, for example with component (I)-2 (see below), and has an excellent stability on storage.

4.2 Preparation of components (I)-2

30 parts of the pigment paste prepared according to section 3.2 are thoroughly mixed with 40 parts of the aqueous polyurethane resin dispersion prepared according to section 2. and 30 parts of deionized water. A component (I) is obtained which is readily meterable, can be mixed readily with components (I) pigmented with other colors, such as with component (I)-1 (see above), and has a very good stability on storage.

5. Preparation of a component (II) according to the invention

35.5 parts of deionized water, 1.5 parts of butyl glycol, 0.5 part of a commercial antifoam and 5 parts of a 3.5% strength solution of a commercial polyacrylate thickener in water are added with stirring to 57.5 parts of a preswollen aqueous paste containing 3% by weight of an inorganic sodium-magnesium phyllosilicate thickener and 3% by weight of polypropylene glycol having a number-average molecular weight of 900, the percentages being based on the overall weight of the paste. The component (II) prepared in this way is very readily miscible with the components (I)-1 and (I)-2 prepared according to section 4.1 and section 4.2, and has an excellent stability on storage.